RESTRICTED ROTATION IN NAPHTHALENIC OLEFINS

BY

LAURENCE OSCAR BINDER, JR.

B.A., Wesleyan University, 1936

M.A., Wesleyan University, 1938

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
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INTRODUCTION

Numerous properly substituted biphenyls which are optically active, due to restricted rotation, have been prepared and resolved, permitting the estimation of the relative sizes of various atoms and groups. However, neither in the biphenyl series nor in the series of aryl olefins prepared by Adams and his coworkers[1,2] has a direct comparison of the =CH— and —CH_3 groups been possible. The work on naphthalenic olefins was undertaken with this end in view.

Successful resolution of β-chloro-β-(2-methyl-1-naphthyl)-acrylic acid and β-chloro-β-(2-methyl-1-naphthyl)-α-methylacrylic acid indicated the advisability of reinvestigating a series of methoxynaphthalenes, one of which, β-bromo-β-(2-methoxy-1-naphthyl)-α-methylacrylic acid, had been prepared by McGrew[3] and been found to be unresolvable.

EXPERIMENTAL AND DISCUSSION OF RESULTS

β-Chloro-β-(2-methyl-1-naphthyl)-acrylic acid and β-chloro-β-(2-methyl-1-naphthyl)-α-methylacrylic acid have been prepared by the following series of reactions: 1-bromo-2-methylnaphthalene → 2-methyl-1-naphthoic acid → 2-methyl-1-naphthoyl chloride → 2-methyl-1-acetonaphthalene and 2-methyl-1-propionaphthalene → β-keto-β-(2-methyl-1-naphthyl)-acrylic acid and β-keto-β-(2-methyl-1-naphthyl)-α-methylacrylic acid → β-chloro-β-(2-methyl-1-naphthyl)-acrylic acid and β-chloro-β-(2-methyl-1-naphthyl)-α-methylacrylic acid.

The two acids were resolved through their respective *d*-α-phenylethylamine and quinine salts. The half-life period of the first, measured in boiling *n*-butanol, is in the neighborhood of seventy minutes, and of the second, about seventy hours. These figures in comparison to the values obtained by Miller[4] for the corresponding mesitylene derivatives—two hundred minutes and no racemization—indicate that the =CH— group causes less restriction of rotation than a —CH_3 group.

In extending the series of methoxynaphthalenes, it was found possible to prepare the geometric isomer of β-bromo-β-(2-methoxy-1-naphthyl)-α-methylacrylic acid, which was made previously by McGrew, by converting it to 3-bromo-2-methyl-4,3-β-naphthopyrone and then hydrolyzing the pyrone ring and remethylating. This

second form was assigned the *cis* configuration by analogy to the work of Perkin[5] and Fittig[6] who synthesized the *cis* and *trans* forms of *o*-methoxycinnamic acid..

It was found possible to prepare only one form of β-bromo-β-(2-methoxy-1-naphthyl)-α-ethylacrylic acid since both isomers of β-(2-methoxy-1-naphthyl)-α-ethylacrylic acid gave the same product, 3-bromo-2-ethyl-4,3-β-naphthopyrone, on bromination.

β-Bromo-β-(2-ethoxy-1-naphthyl)-α-methylacrylic acid was also prepared, but the resolvability of none of the members of this series has been investigated thoroughly. Preliminary trials with quinine and *d*-α-phenylethylamine in the case of the *trans* forms of β-bromo-β-(2-methoxy-1-naphthyl)-α-methylacrylic acid and β-bromo-β-(2-ethoxy-1-naphthyl)-α-methylacrylic acid have given no indications that they could be obtained optically active.

SUMMARY

β-Chloro-β-(2-methyl-1-naphthyl)-acrylic acid and β-chloro-β-(2-methyl-1-naphthyl)-α-methylacrylic acid have been prepared and resolved. Their half-life periods in boiling *n*-butanol indicate that the =CH— group has less effect than the —CH_3 group in restricting rotation.

The *cis* and *trans* forms of β-bromo-β-(2-methoxy-1-naphthyl)-α-methylacrylic acid, one form of β-bromo-β-(2-ethoxy-1-naphthyl)-α-methylacrylic acid, and one form of β-bromo-β-(2-methoxy-1-naphthyl)-α-ethylacrylic acid have been prepared, but their resolvability has not been fully investigated.

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VITA

The author was born February 19, 1915, in Englewood, New Jersey. He spent his early years in Leonia, New Jersey, and attended the public schools of that town. In 1932, he entered Wesleyan University, from which he received the Bachelor of Arts degree in 1936. He held a position as graduate assistant there from 1936-38, receiving the Master of Arts degree in 1938. In the fall of 1938 he entered the Graduate School of the University of Illinois and held a graduate assistantship for the years 1938-39 and 1940-41.

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